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To: Dr. D. Mills,
Director of Research

Corrosion Chemistry and Decontamination Project Group
1987 Year-end Review and 1988 Work Program

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The results and achievements of the Corrosion Chemistry and Decontamination Project Group in 1987 are reviewed and the direction of its work program in 1988 is outlined. The Group's efforts are mainly in the areas of steam generator corrosion and cleaning, corrosion inhibitor development and activity transport.

INTRODUCTION

This report presents an overview of the Corrosion Chemistry and Decontamination Project Group (CCDPG), the results it has achieved in 1987 and the direction that its work program will take in 1988.

The CCDPG was created in 1986. It had previously been a part of the then Environmental and Inorganic Chemistry Research Section (currently the Process Chemistry Section). The mission of the group is to carry out R&D and technical investigations on the chemistry and control of corrosion, chemical cleaning and decontamination processes.

The main area in which the group contributes is the Steam Generator Corrosion Program. Degradation of steam generator (SG) tubes resulting in leaks of the primary coolant are a major concern in the operation of pressurized water reactors. Although Ontario Hydro's CANDU reactors have been world leaders in steam generator integrity, a long-term research program is being carried out to anticipate problems which may occur and develop remedial measures to avoid or minimize the consequences of these problems. Studies related to SG integrity constituted approximately 75% of the group's 1987 work program budget of $936K. In addition to the SG work, the group has a substantial effort underway on the identification and testing of new corrosion inhibitors for use with the CAN-DECON decontamination process, and has started a small project on activity transport in primary heat transport (PHT) systems.

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In 1987, the work program of the CCDPG was approximately 38% transfer-funded. The main client was the Technical and Training Services Division (TTSD), principally the Central Nuclear Services Department, while Nuclear Generation Division and Design & Development-Generation also provided some funds. In 1987, the CCDPG undertook its first project on behalf of the CANDU Owners Group (COG). This source of funding will grow in importance in 1988 as three additional proposals have been approved for funding during the 1988-89 COG fiscal year. The need to satisfy the requirements of the COG projects will have a substantial impact on the ability of the group to respond to short-term requests for assistance from other client groups.

The staff in the CCDPG at year end 1987 is shown in Table 1, while internal reports and external publications are listed in Tables 2 and 3, respectively. In the following sections, the major elements of the work program will be discussed in terms of accomplishments in 1987 and objectives for 1988.

STEAM GENERATOR CORROSION PROGRAM

Corrosion and Chemistry in Confined Regions

The greatest risk to our SGs is the formation of chemically aggressive conditions in regions of restricted flow. Boiling in these areas causes non-volatile impurities to accumulate and produces localized chemistry conditions vastly different from those in the bulk water. The most important of such confined regions is under the sludge which accumulates on the secondary face of the tubesheet and in crevices at the support plates.

The rate at which contaminants concentrate under tubesheet sludge piles has been studied in laboratory autoclaves for several years and a model has been produced to describe this process as a function of the heat flux and the properties of the sludge. This model was described in a paper published in the Nuclear Journal of Canada in 1987. These studies were carried out using electrically-heated test probes. To more closely simulate the situation in an operating steam generator, a loop was constructed in which the SG tube test specimen is internally heated by a fluid at the temperature of the PHT system. The construction and commissioning of the loop were completed in 1987, and a three-year project (co-funded by COG) was undertaken to study the dependence of concentration and deconcentration rates of solutes on factors such as sludge pile depth, composition and porosity, and on the available superheat.

Studies continued in laboratory and station autoclaves to determine the nature and severity of under-deposit corrosion attack on steam generator tube materials. While in previous years these studies had concentrated mainly on the effects of condenser in-leakage on the alloys Inconel 600 and Monel 400, emphasis in 1987 was shifted to the Incoloy 800 tube material

which will be used at Darlington and for which there is relatively little in-service experience available. The first two of a series of refreshed autoclave tests in which Incoloy 800 tube probes are exposed to water chemistry faulted with Lake Ontario water and dissolved oxygen were carried out. This work will be continued in 1988 with funding by COG.

A water-treatment plant malfunction in 1986 allowed sulphuric acid to enter all the steam generators at Bruce A. Five tubes were removed from SG 3 of unit 1 in January 1987. The deposits on these tubes were extensively examined and found to contain high concentrations of sulphate, and regions of copper-rich deposits. There were areas of shallow attack on all the tubes, and the oxide layer in these areas appeared to be somewhat depleted in chromium. Further tube removal was recommended to determine the rate of propagation of the attack and to characterize the extent of damage in the other units. In addition, a COG-supported project will be initiated in 1988 to systematically study the effect of chemical excursions caused by water-treatment plant upsets on steam generator tube materials. This work will include scoping experiments in isothermal test capsules to provide preliminary information on the effect of a broad range of chemistry and material conditions, followed by extended autoclave exposures under heat flux conditions in order to simulate plant conditions as closely as possible.

Work continued in 1987 on the development of the high temperature electrochemical corrosion monitoring system. Construction was completed of a dedicated electrochemistry laboratory in room KR 018. Software was written for carrying out DC and AC techniques completely under computer control. One of the major difficulties in carrying out high temperature electrochemistry is the unavailability of a robust, reliable high-temperature reference electrode. A design was obtained for a new type of epoxy-filled high temperature electrode developed at SRI International and assembly of a prototype was started.

In 1988, a high temperature potentiostatically-controlled technique will be developed to conduct accelerated corrosion experiments in normal and abnormal SG chemistry environments. The capability will be developed to obtain high temperature AC impedance spectra and numerical methods will be developped for their analysis. Use of an AC impedance method for the measurement of solution conductivity at high temperature will be investigated.

Chemical Cleaning and Water-jetting

It may be necessary to remove the deposits which have accumulated in a steam generator if under-deposit corrosion threatens the integrity of the materials or if fouling of heat transfer surfaces results in a reduction of the power output of the reactor. Deposit removal can be accomplished in two ways:

chemical cleaning or water-lancing. Work was carried cut in 1987 in both of these areas, primarily in chemical cleaning.

At Bruce NGS, the configuration of the SGs precludes the use of water-jetting and chemical cleaning is currently the only option for deposit removal. A multi-year program to develop solvents capable of chemically removing the deposits is nearing completion. In 1987, strategies were developed for make-up of the solvent constituents during a station application. It was found that replenishment of the EDTA in the copper-removal solvent is not required and that make-up of the ethylenediamine is sufficient to restore the effectiveness of the process. Larger-scale tests will be carried out in 1988 in the chemical cleaning loop to further optimize the make-up strategy for ethylenediamine.

During a chemical clean of a Bruce SG, the solvent will flow at relatively high velocities through the blowdown lines. Tests were carried out in 1987 to define the process conditions which will avoid erosion/corrosion in the carbon steel portions of the blowdown lines. It was found that the concentration of corrosion inhibitor in the iron removal solvent was an important factor. In the absence of inhibitor, flow-assisted corrosion resulted in through-wall penetration of a carbon steel weld in 7 days, while there was no evidence of any flow-related attack at the normal inhibitor concentration of 1%. In 1988, an analytic method will be developed to monitor the inhibitor concentration during chemical cleaning.

Testing was completed in 1987 of the corrosion of welds during and after a SG chemical clean. It was found that while some preferential weld corrosion was produced by the chemical cleaning process, the degree of attack was tolerable. Extended exposure of cleaned specimens to simulated steam generator conditions failed to produce any further enhanced corrosion. The materials tested to date include only those present below the first support plate in a Bruce steam generator, since the work was carried out in anticipation of sludge-pile removal which would only involve a partial fill of the SG. In late 1987, interest developed in a full-vessel clean as there were indications that fouling may be affecting the heat transfer capability of the Bruce "A" SGs. In 1988, the corrosion and process concerns associated with a full-vessel clean will be evaluated and programs initiated to address them.

Water-jetting tests carried out by TTSD at Pickering Unit 1 in early 1987 were only partly successful and a program was initiated by TTSD to enhance the effectiveness of the water-jetting procedure. One of the options being evaluated is the use of an additive called SUPERWATER to improve the cohesiveness of the water stream. In support of this work, a series of isothermal capsule tests was carried out to evaluate the corrosion implications of the use of this additive during subsequent SG operation. There was

no sign of any deleterious corrosion effects. During the course of this work, it was found that the viscosity of a SUPERWATER-containing solution is strongly dependent on its ionic strength. Use of deionized water results in unfavourable solution characteristics, and better results were obtained with untreated tap water. This phenomenon will be further studied in 1988.

Secondary Circuit Chemistry and Particulate Transport

The most effective means of avoiding under-deposit corrosion is to minimize the formation of the deposits in steam generators. These deposits are formed mainly from the low levels of impurities which are produced by corrosion of the secondary system pipework and which enter the steam generator with the feedwater. As part of a long-term program to identify and ultimately control the major sources of these impurities, studies are being carried out in the areas of corrosion product transport in the secondary circuit, condensate/feedwater chemistry optimization and lay-up chemistry.

The concentration and detailed composition of particulate corrosion products in the secondary circuit are poorly known. Samples of corrosion products collected from various points in the secondary system were examined and several forms of iron oxide were detected. In order to more systematically study the movement of corrosion products, equipment was assembled and installed in Bruce NGS "B" Unit 7 to collect water from eight points in the secondary system, cool and depressurize it and pass it through a 0.45 um filter membrane and ion exchange membrane. Sampling will be carried out in 1988 at normal operating conditions, and during transients such as start-ups, shut-downs, and load maneuvers. The objective of the work will be to establish the amount and origin of the suspended and dissolved corrosion products in the system.

A major limitation of our current sampling capability is the need to cool the sample before filtration. Precipitation and other chemical reactions in the sample lines may alter the amount or chemical nature of the material collected on the filter membrane. To further assess the impact of cooling the samples, specifications were completed in 1987 for a sampling module capable of filtering secondary system water without prior cooling. One such module will be procured in 1988, with the intention of comparing the results of high- and low-temperature filtration carried out at the same point in the system at the same time.

Long-term wet lay-up of system components is a potential source of corrosion products in the secondary circuit. A program was started in 1987 with the objective of improving chemistry control during extended lay-ups such as those required for LSFCR. A project was initiated to determine the reasons for the rapid decomposition of hydrazine to ammonia in the Pickering Units 1

and 2 boilers and this work will be completed in 1988. An alternative oxygen scavenger, VOS-68, was evaluated to replace hydrazine.

A long-term objective of the CCDPG's work program is to develop a detailed understanding of the chemistry control in our secondary circuits, and to test alternative pH-control and oxygen scavenging agents which may be superior to the currently-used chemistry regime for minimizing corrosion. The first element of this work will be a COG-funded project to study the behaviour of morpholine under CANDU conditions. Its decomposition reactions and their effects on system corrosion will be studied. The experimental work will be carried out mainly in a Model Boiler test loop assembled during 1987, and will begin in April 1988 following final loop commissioning.

DECONTAMINATION AND ACTIVITY TRANSPORT

The reduction of radiation fields in the vicinity of the reactor face will continue to be a requirement to support major maintenance efforts such as LSFCR. Studies were carried out in 1987 to improve the effectiveness of the CAN-DECON decontamination process and to investigate the reasons for the unexpectedly rapid activity transport at Bruce NGS "B".

Decontamination

A major development requirement of the CAN-DECON decontamination process continues to be a sulphur-free inhibitor. The inhibitor employed during the successful decontaminations at Pickering NGS, Rodine 31A, contains 7% sulphur in the form of sulphuric acid and substituted thioureas. Residual sulphur contamination left in the PHT system could be detrimental to Inconel 600 steam generator tubes, and the use of Rodine 31A is considered unacceptable at Bruce NGS. A critical literature review in 1986 identified three promising sulphur-free alternatives, and detailed laboratory evaluations of the three candidates were continued in 1987 through a collaborative effort by workers at OHRD, the University of Guelph (U of G) and AECL-Chalk River. Weight-loss studies at OHRD showed that inhibitor efficiencies of 50-90% are observed at an inhibitor concentration of 0.1%, and that galvanically coupling carbon steel to 410 stainless steel did not diminish the effectiveness of the inhibitors. It was found, however, that different grades of carbon steel corroded at quite different rates, particularly in inhibited solutions, indicating that test results obtained on materials other than the A106B carbon steel used for the feeder pipes may be significantly in error. Electrochemical studies being carried at the U of G showed that the inhibitors function principally by inhibiting the anodic iron-dissolution half-reaction rather than the cathodic hydrogen-evolution reaction.

In 1988, studies at OHRD will evaluate the effect of factors such as dissolved iron and a magnetite surface coating on the effectiveness of the inhibitors. Work at the U of G will study the corrosion process in greater detail and determine the order of the corrosion reaction with respect to the constituents of the CAN-DECON reagent in the presence and absence of corrosion inhibitors. The scope of the studies at the U of G is being expanded through a grant from the Natural Sciences and Engineering Research Council for the hiring of a post-doctoral fellow by the University. The expanded program will further investigate fundamental mechanisms of corrosion inhibition at carbon steel surfaces under decontamination chemistry conditions.

Minor technical evaluations of several commercial corrosion inhibitors were also carried out during 1987 in support of chemical cleaning applications in heat exchangers and fossil-fired boilers.

Activity Transport in Primary Circuits

Radiation fields at the reactor face of the Bruce "B" units have increased at an unexpectedly high rate during early unit operation. The fields are due to the isotope Co-60. Support was provided to the station in 1987 in chemically and radiochemically analysing system "crud" samples and in identifying design and operating characteristics which may be responsible for the different behaviour of the Bruce "A" and "B" reactors. This work will be extended in 1988 to include examination of samples from other reactors to better characterize the circulating particulates in PHT systems. This work may be relevant to the study of pressure tube degradation by providing some information on the zirconium content of PHT particulates, which may be related to the spalling of oxides from pressure tubes.

ACKNOWLEDGEMENTS

The accomplishments described in this report are the result of the dedication and hard work of all the members of the group. Their individual contributions to meeting the challenge of maintaining our long-term research programs while also solving problems of a more immediate nature are gratefully acknowledged.

Approved by:

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TABLE 1

Staff of the Corrosion Chemistry and Decontamination Project Group as of Year End 1987

Dr. P. Spekkens	(Paul)	Project Manager
Dr. F. Gonzalez	(Paco)	Associate Research Engineer
Ms. A.M. McKay	(Sandy)	Engineer
Dr. T.W. Ng	(Wing)	Engineer
Dr. J.M.T. Raycheba	(John)	Chemist
Mr. P. McSweeney	(Peter)	Chemist
Mr. D.S. Mancey	(Dave)	Chemist (temporary)
Mr. L.O. Gibson	(Larry)	Technician
Mr. P. Leung	(Patrick)	Technician
Mr. A.C. McBride	(Al)	Technician
Mr. E.P. McNeill	(Gene)	Technician
Mr. G. Till	(Grenville)	Technician

TABLE 2

RESEARCH DIVISION REPORTS ISSUED IN 1987

Report Number	Title and Author	File Number	Date Issued
Category A			
86-350-K	Flowpath Optimization for Bruce "A" Steam Generator Chemical Cleaning A.M. McKay	836.3332	April 23, 1987
86-347-H	A Chemical Cleaning Solvent for Removing Magnetite from Nuclear Steam Generators P. McSweeney	836.333	April 16, 1987
87-47-H	Candidate Organic Corrosion Inhibitors for Use in CAN-DECON Decontaminations-Summary of 1986 Results J. Raycheba	836.29	April 24, 1987
87-137-H	Computer-controlled Electrochemistry DC Techniques J. Raycheba	836.333	June 26, 1987
87-203-H	Decontamination Inhibitor Development - Corrosion of A106B Carbon Steel and 410 Stainless Steel Galvanic Couples in a CAN-DECON Solvent J. Raycheba	836.29	August 20, 1987
87-275-H	Computer-controlled Electrochemistry - AC Techniques J. Raycheba	836.333	December 2, 1987
Category B			
C87-9-K	Boiler Tube Deposits - Lambton Unit 1 P. McSweeney	836.333	February 16, 1987
C87-21-K	Water Wall Tube Deposits - Lakeview Unit 2 P. McSweeney	836.333	March 13, 1987
M87-43-K	Recent EPRI Steam Generator (SG) Reliability Project Meetings P.C. Lichtenberger and P. Spekkens	827.27	April 30, 1987
C87-44-K	Boiler Tube Deposit - Manitoba Hydro P. McSweeney	836.333	June 2, 1987
C87-40-K	Chemical Cleaning of Water Wall Tube P. McSweeney	836.333	June 11, 1987
C87-54-K	Boiler Tube Deposits - Lambton Unit 2 P. McSweeney	836.333	June 22, 1987
C87-56-K	Examination of Deposits from Heat Transport Motor Cooling System, Bruce NGS 'B', Unit 6 P. McSweeney	836.3332	June 14, 1987
C87-57-K	Particulate Loading of Water Lance Filters from Pickering NGS A.C. McBride	836.3332	July 14, 1987
C87-46-K	Evaluation of FORMAC 130 Inhibitor P. McSweeney	836.333	June 29, 1987
C87-82-K	Symposium on Chemistry in High Temperature Aqueous Solutions A.M. McKay	830.5	October 2, 1987
C87-106-H	Evaluation of Corrosion Inhibitors P. McSweeney	836.333	December 21, 1987

TABLE 3

External Publications in 1987

Authors	Title	Journal or Conference	Date
F. Gonzalez and P. Spekkens	Concentration Processes under Tubesheet Sludge Piles in Nuclear Steam Generators	Nuclear Journal of Canada	Vol 1 No 2 p. 129 June 1987
F. Gonzalez and O. Trass	A Shock Tube Study of the Pyrolysis of Nitric and Nitrous Oxides	Proceedings of the 16th Shock Tube and Wave Symposium Aache, West Germany	July, 1987